



TITLE:

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Rheology of Diblock Copolymer Systems

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AB diblock copolymers exhibit various microdomain structures and thus offer a rich field of rheology. In a low molecular weight, B-selective solvent, the AB diblock copolymers form regular lattices of micelles with A cores and B corona and exhibit plasticity. On the other hand, in polymeric B-selective solvents, homo-B chains, the copolymer micelles are randomly dispersed and viscoelastic relaxation prevails. Those AB/B blends exhibit fast and slow relaxation processes. The fast process is attributed to relaxation of individual corona B blocks tethered on the A cores, while the slow process is related to diffusion of the micelles.

Keywords: Block Copolymer / Plasticity / Relaxation / Entanglement / Tube Model / Diffusion

Chemically different polymer chains usually segregate with each other and their blends contain phase-separated domain structures. In block copolymers such segregating polymeric blocks are chemically connected at their ends, resulting in the domains restricted in the molecular dimension of the constituent blocks. This structure, called a microdomain structure, changes with the molecular weights and composition of the blocks as well as with the copolymer concentration (in the cases of solutions and blends). Various properties of the copolymer systems are strongly influenced by such microdomain structures. For styrene (S)-isoprene (I) and S-butadiene (B) diblock copolymers, we have found that their solutions exhibit unique rheological features that change with the nature of the solvents [1-4]. These features are summarized below in relation to the domain structures in the solutions.

In an I-selective, low molecular weight solvent, n-

tetradecane (C14), SB and SI diblock copolymers form micelles with precipitated S cores and solvated B and/or I corona. When the copolymer concentration is above a critical concentration for micelle overlapping, the micelles exhibit anomalous rheology that is characterized with highly nonlinear stress (σ) - strain (γ) patterns observed in dynamic tests using slowly oscillating strain. As an example, Figure 1 shows typical patterns found for a SB/C14 solution against small and large amplitude (γ_0) strain [1,2].

In Figure 1, a rectilinear pattern indicating a proportionality between σ and γ is observed for small γ_0 while a distorted, lozenge-shaped pattern is seen for large γ_0 . These patterns characterize plasticity of the system: The proportionality between σ and γ indicates elastic behavior of the solution before yielding, and the lozenge-shaped pattern corresponds to elastic deformation and successive plastic flow repeated twice (in the opposite direction) during one

FUNDAMENTAL MATERIAL PROPERTIES — Molecular Rheology —

Scope of research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.



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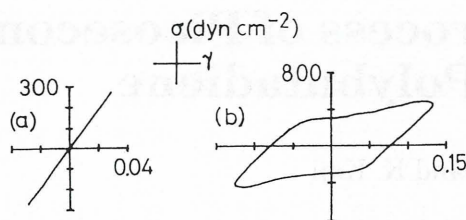


Figure 1. Stress-strain patterns at $\omega = 0.0524 \text{ s}^{-1}$ obtained for a 20wt% C14 solution of a SB diblock copolymer ($M_S = 16K$, $M_B = 36K$).

cycle of oscillatory strain. The plasticity of the solution is confirmed also in its steady flow behavior [1,2].

Small angle x-ray scattering (SAXS) measurements indicate that the plasticity of SB copolymer micellar solutions is due to a regular, cubic lattice of the micelles [1,2]. This lattice, called a macrolattice, does not flow but deforms elastically for stresses smaller than the lattice strength (yield value), thereby providing plasticity to the solution.

The macrolattice formation is considered to result from compromise of contradicting thermodynamic requirements, an osmotic requirement for maintaining uniform B segment concentration profile in the C14 matrix phase and an elastic requirement of randomized B block conformation [1,2]. This hypothesis is confirmed from several experimental facts, including a fact that the micelles are preserved but the macrolattice is disordered in polymeric B-selective solvents, homo-B (hB) chains [1,2]: In the SB/hB blends, the uniform B segment concentration profile in the matrix is maintained irrespective of the B block conformation and the two requirements are no longer contradicting with each other.

As explained above, the SB/hB blends contain randomly dispersed micelles and exhibit linear viscoelastic relaxation characterized with elliptic σ - γ patterns, as is the case also for homopolymer systems [1-3]. However, the relaxation behavior of the blends is not very similar to that of homopolymers. As an example, Figure 2 shows frequency dependence of storage moduli G' for a series of SB/hB blends with the SB concentration as indicated [3]. The sample code numbers indicate molecular weights in unit of 1000. The SB micelles exhibit fast and slow relaxation processes (cf. diamonds and arrows) at time scales where the matrix hB has relaxed (dashed curve).

For the fast process, the reduced dynamic moduli scaled with the B block molecular weight M and concentration c , $G_r = [M/c]G^*$, exhibit universal relaxation mode distribution [3]. In addition, for concentrated micelles entangled through their B blocks, the relaxation time for the fast process increases exponentially with increasing c and M [3]. These features are similar to those for relaxation of branched homopolymers (stars), suggesting that the fast process of the micelles are attributed to relaxation of

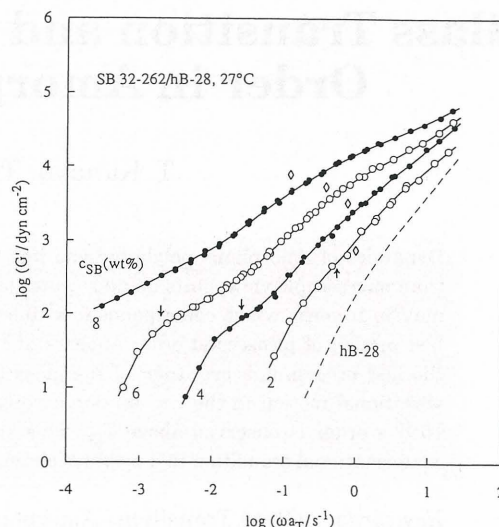


Figure 2. Frequency dependence of storage moduli for a series of SB/hB blends with the SB concentration as indicated.

individual corona B blocks. This assignment is strongly supported from results of stress relaxation measurements that a damping function for the fast process is in good agreements with the functions for homopolymer systems [4]. However, quantitatively, the relaxation time of the B blocks is 10^3 - 10^5 times longer than that of the corresponding star hB chains [3]. Analysis in terms of tube model suggests that the spatial confinement for the B blocks due to the impenetrable S cores (not existing for star hB) is the main cause for this quantitative difference in the relaxation times [3].

For the slow relaxation process of the micelles, the reduced moduli G_r do not exhibit the universal mode distribution [3]. In addition, in the nonlinear stress relaxation behavior, the slow process exhibits much stronger damping as compared to the fast process [4]. These facts indicate that the two processes have different molecular origins. For entangled micelles the relaxation time for the slow process was close to an estimated Stokes-Einstein (SE) diffusion time, suggesting that the slow process reflects motion of the micelle as a whole [3]. However, for dilute and nonentangled micelles, the relaxation time for this process is much shorter than the SE diffusion time [3]. The mechanism of the slow process for this case is now being investigated.

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